

From pockets to channels: Density-controlled diffusion in sodium silicates

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Classical molecular dynamics is used to study the dynamics of sodium atoms in liquid $\text{Na}_2\text{O}-3\text{SiO}_2$ (NS3) as a function of system density. It is found that diffusion displays different régimes with increasing density at fixed temperature: a channel-connected network at ambient pressures which reduces to small pockets once the density is increased. The obtained features can be further characterized by the probability of Na hopping that shows a percolative behavior at around 2.25 g/cm^3 at the lowest temperature of 1500 K, which correlates with a threshold in the coordination number of the silicon and oxygen atoms. These results highlight the fact that transport properties in simple silicates can be substantially modified under a limited density change.

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I. INTRODUCTION

Silicates are the major components of magmatic liquids and their behavior under various thermodynamic conditions (pressure, temperature, and composition) have therefore received an important interest over decades.^{1,2} Among such properties, transport properties of magmas intimately relate to the physical, chemical, and climatological evolution of the Earth's mantle and its surface. However, despite intensive studies in recent years,^{3,4} little is known about the flow mechanism and the diffusion of chemical species in response to the important pressure that is applied at gigapascal values.

Sodium silicates have been extensively studied both from the experimental and theoretical sides.⁵ The addition of sodium usually disrupts the basic silica network by creating so-called nonbridging oxygen (NBO), having, in their immediate vicinity, a sodium cation, and whose fraction can be quantified as a function of Na composition.⁶ This results in a global softening of the glass network that manifests in a rigid to flexible transition at the critical concentration of 20% soda.^{7,8} For larger compositions, flexibility promotes ionic conduction as local pathways are possible because of the presence of local deformation (floppy) modes.⁹

Of particular interest is that the Na diffusion does not take place in a random fashion but along preferential paths that have been inferred from extended x-ray absorption spectroscopy^{10,11} and extensively characterized from molecular dynamics simulations and inelastic neutron scattering.^{12–14} This has led to the identification of the so-called channel diffusion also popularized by the modified random network model of Greaves.^{15,16} On the other hand, little is known about such dynamical properties in densified silicates. While there has been some studies on the structural changes induced by pressure with observed salient features, such as the growth of silicon and oxygen coordination numbers,^{17,18} it has been reported only that the network-forming ions (oxygen) were displaying a diffusivity maximum¹⁹ with pressure, an anomaly that bears some striking similarities with the one found in liquid silica²⁰ and liquid water.²¹ The change of Na diffusion in a 7% densified $\text{Na}_2\text{O}-3\text{SiO}_2$ glass has been investigated by Zhang and coworkers,²² and these authors have suggested that the observed changes in the activation energy for diffusion could be attributed to a change in the pathways for ionic

migration. On related systems (Mg silicates), it was shown from first-principles molecular dynamics that the diffusion properties were highly sensitive to pressure and temperature.²³

Here, we attempt to address this basic issue (sodium diffusion in densified silicates) and report on the dynamic properties with changing densities and temperatures using molecular dynamics. It is found that along an isotherm, the diffusion constant D_{Na} displays three approximate régimes: A first one at low density in which D_{Na} is found to be nearly constant. For densities larger than a certain threshold value $\rho_{c1}(T)$, a sharp decrease is obtained, followed by an even more pronounced decrease at very high density. No Na diffusivity anomaly is found.

The analysis reveals that in the high-density régime, the motion is restricted to small pockets of size $5 \text{ \AA}$ on the picosecond time scale, with diffusion setting on at nanoseconds only. The size of these pockets tends to grow with decreasing ρ as does the spatial extent of Na motion, and these ultimately percolate into the channels found at ambient pressure. The trends with ρ can be correlated with changes in structure and highlight the crucial role played by thermodynamic conditions (ρ but also temperature) in the transport properties of model silicates.

II. SIMULATION DETAILS

The system we have been considering is a $N = 3000$ atom $\text{Na}_2\text{O}-3\text{SiO}_2$ (NS3) system containing 750 silicon, 500 sodium, and 1750 oxygen atoms, being placed in a cubic box of various lengths to obtain the desired density. The length $L = 32.39 \text{ \AA}$ allows us to recover the experimental density²⁴ $\rho = 2.37 \text{ g/cm}^3$ and corresponds to a computed pressure of $P = -1.9 \text{ GPa}$. The interaction potential is a two-body Teter potential²⁵ that has been extensively used for the structural, topological, and thermodynamical properties^{26–28} of sodium silicates with changing compositions. Alternative potentials have been proposed²⁹ for the study of the same system but most of them lead to the same results (for a critical comparison of certain structural quantities; see, however, Ref. 30). The effect of density on such systems using a classical potential has been considered¹⁸ only in a high-temperature liquid for the NS4 silicate with a Born-Mayer interaction potential fairly

similar to the one used here. While one may wonder about the reliability of such potentials to account for the description of silicates under pressure, we have checked that a certain number of salient features observed experimentally^{5,17} were recovered from our simulations: (i) reduction of the bond lengths with increasing density, (ii) silicon coordination number change from four to five to six (we obtain $n_{\text{Si}} = 4.5$ at $P = 17.7$ GPa and 1500 K), and (iii) broadening of the structure factor $S(Q)$ with a significant reduction of the first sharp diffraction peak. Beyond these encouraging results, the main question is to know to what extent fixed charges can be considered in an interaction potential with increasing density. At ambient pressure, the use of a Coulomb interaction with fixed partial charges is simply the result of the ionic character of the interactions present, and the absence of charge transfer during the simulation. While we are not aware of any report of densified silicates, a recent *ab initio* molecular dynamics study (where the electrons and charge transfer are treated explicitly) on an oxide network-forming glass under high pressure^{31,32} has shown that the deformation of the electronic cloud is still small enough so that there is no need to modify the pseudopotentials designed for ambient pressures. Nevertheless, one cannot be 100% sure in the reliability of empirical potentials at very high pressures, but the present example^{31,32} suggests that a certain degree of confidence can be expected.

After having equilibrated the liquid at fixed density and 6000 K for 1 ns (time step 1 fs and integration using a Verlet algorithm), we have cooled the system in the micro-canonical ensemble to various (T, ρ) conditions of interest. In the following, we have focused on the long-time dynamic properties of the system, and mostly on the Na dynamics as it appears that its diffusion constant is two orders of magnitude larger than the one of silicon or oxygen. This difference tends to decrease with increasing temperature but remains significant. In most of the situations, the diffusive régime (linearity of the mean-squared displacement in a log-log plot) could be unambiguously determined. For systems with high density, however, there was need to extend runs up to several nanoseconds. Finally, for systems at the very limit of the region of investigation ($T \simeq 1500$ K, $\rho = 4.5$ g/cm³), it was difficult to extract a meaningful number for the diffusion constant D_{Na} .

III. RESULTS

Figure 1 shows accumulated snapshots of 15 Na atoms at $\rho = 2.0$ and 4.0 g/cm³ for $T = 1500$ K over a time interval of 20 ps. The upper panel highlights simply the general accepted picture of a SiO₂ rigid matrix in which the sodium motion is achieved through preferential paths,^{12,13} leading to the “channel dynamics.” These paths can be clearly seen in Fig. 1: within the fixed time frame (20 ps), entire regions contain a large number of Na atoms (even though it is 2D projected), whereas other regions are indicative of the silica-rich structure with only a few or no sodium present. On the opposite, at high ρ , the global picture differs completely in appearance with isolated pockets separated by a mean distance of 6 Å. Diffusion takes off at long times ($t \simeq 2$ ns), after a substantial time spent in a caging régime (10 ps to 2 ns), identified with back-and-forth hops inside a Na-rich pocket.

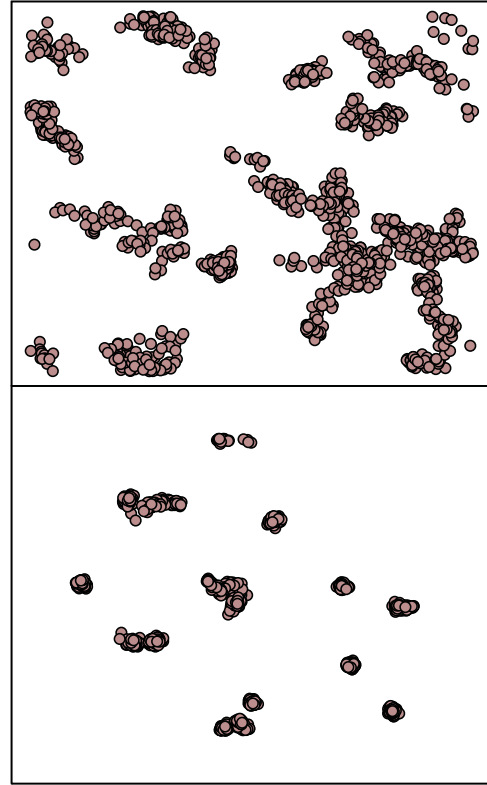


FIG. 1. (Color online) Accumulated trajectories over $t = 20$ ps at 1500 K of 15 sodium atoms in the NS3 system for $\rho = 2$ g/cm³ (top panel) and $\rho = 4$ g/cm³ (bottom panel).

Figures 2 and 3 represent the diffusion constant D_{Na} obtained from the long time limit of the mean-squared displacement via the usual Einstein equation:

$$D_{\text{Na}} = \lim_{t \rightarrow \infty} \frac{1}{6t N_{\text{Na}}} \sum_{i=1}^{N_{\text{Na}}} \langle |r_i(t) - r_i(0)|^2 \rangle. \quad (1)$$

Results are shown as a function of density for various isotherms ranging from 1500 K to 4500 K. It should be noted that D_{Si} and D_{O} display a diffusivity anomaly (Fig. 2) very similar to the one found in liquid silica²⁰ and liquid water.²¹

Coming back to the sodium motion, we obtain three clear régimes for the diffusion: a first one at low density $\rho < \rho_{c1}(T)$ where D_{Na} is nearly constant and changes only by a factor of 3 in the considered temperature range (1500 K–4500 K). The threshold density $\rho_{c1}(T)$ is found to be lower by 0.1 g/cm³ than the density at zero pressure for nearly all temperatures. When compared to the oxygen and silicon diffusion constant, it becomes obvious that the intermediate régime for Na diffusion is found in the anomalous density region where D_{Si} and D_{O} become maximum. However, the locations of the maxima ($\rho = 2.91$ g/cm³) and minima ($\rho = 2.4$ g/cm³) in D_{Si} and D_{O} are not found to correspond to the régime thresholds obtained for D_{Na} .

When plotted at fixed ρ , we find an Arrhenius behavior $D_{\text{Na}} = D_0 \exp(-E_A/k_B T)$ for the diffusion. It appears that our D_{Na} is in excellent agreement with the experimental results^{34,35} obtained from tracer diffusion techniques and all contrast substantially with previous results from Horbach’s

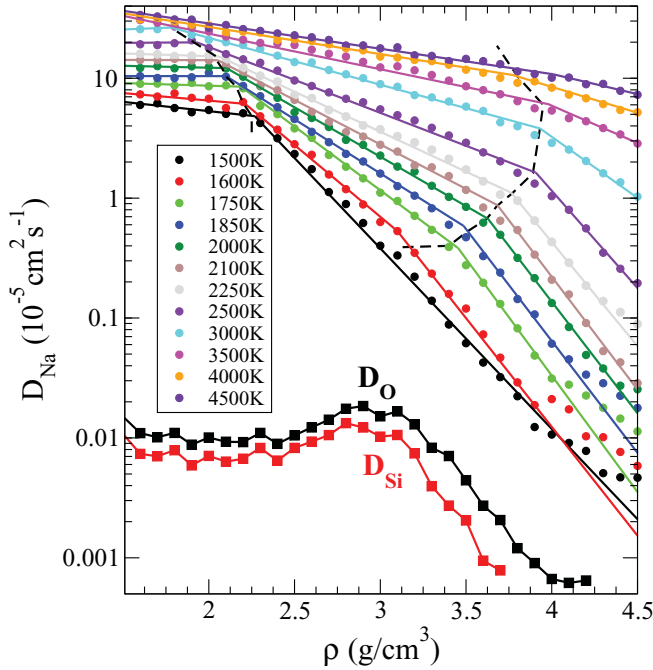


FIG. 2. (Color online) Sodium diffusion constant D_{Na} as a function of density ρ in a liquid NS3 system for various isotherms (circles). Straight lines are guides to the eye. The broken lines serve to define approximately the thresholds $\rho_{c1}(T)$ and $\rho_{c2}(T)$. The bottom (squares) show the oxygen and silicon diffusion constants D_{O} and D_{Si} at 1500 K.

MD simulations.³³ Given the fact that the dynamical properties of liquids are usually very sensitive to the interaction potential,³⁶ the present agreement obtained from the Teter potential reinforces the reliability of the present simulations. The corresponding activation energy is found to be $E_A = 0.43$ eV at $\rho = 2.40$ g/cm³, which is slightly smaller than the one determined by Gupta and King³⁴ (0.70 eV), as observed

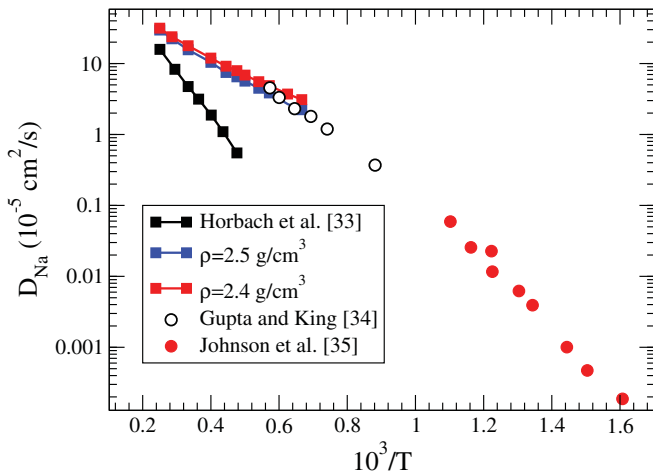


FIG. 3. Sodium diffusion constant D_{Na} as a function of inverse temperature for $\rho = 2.4$ (red squares) and 2.5 g/cm³ (blue squares) compared to other results from MD simulations³³ and to experimental results from Gupta and King³⁴ and Johnson *et al.*³⁵

from the different slopes on Fig. 3. The latter value is in harmony with other experiments ($E_A = 0.73$ eV³⁷) performed in the vicinity of the glass transition (found to be equal⁷ to 480 °C, i.e., $10^3/T = 1.33$). It has been found from conductivity measurements $E_A = 0.73$ eV that contains the Coulomb and the strain part of the activation energy for conduction, the strain part being the one associated with the activation energy for diffusion. For the density $\rho = 2.5$ g/cm³, we obtain $E_A = 0.45$ eV, i.e., $\Delta E_A = 0.02$ eV when compared to the density at ambient pressure, similarly to the results found on densified silicates.²²

A second régime (Fig. 2) appears for $\rho_{c1}(T) < \rho < \rho_{c2}(T)$, for which D_{Na} now decreases much more markedly with density. In the low-temperature limit (1500 K), we obtain a change from 4.5×10^{-5} cm² s⁻¹ to 0.31×10^{-5} cm² s⁻¹ when changing ρ from 2.25 (corresponding pressure -0.8 GPa) to 3.1 g/cm³ (corresponding pressure 8.9 GPa). Similarly, at fixed density changes in D_{Na} appear to be more pronounced with temperature increase. Finally, a third régime is obtained at high density [$\rho > \rho_{c2}(T)$], for which diffusion decreases even more with compaction.

To further characterize the dynamics of these régimes, we use the self part of the Van Hove correlation function³⁸ defined by

$$G_s(r, t) = \frac{1}{N_{\text{Na}}} \sum_{i=1}^{N_{\text{Na}}} \langle \delta(r - |r_i(t) - r_i(0)|) \rangle. \quad (2)$$

The latter allows to determine the probability $4\pi r^2 G_s(r, t)$ that a sodium atom initially ($t = 0$) at $r = 0$ has moved by a distance r during a time t . In Fig. 4, we show $G_s(r, T)$ as a function of the distance for a time $t_0 = 20$ ps at the temperature of 2000 K for various densities. The value of 20 ps is used in forthcoming calculations but we have also considered $t_0 = 100$ ps and checked that the conclusions were consistent, i.e., a scaling (increase) in t_0 leads to a scaling (increase) in the maximal distance covered by the Na ions (L_M , see below).

From Fig. 4, it can be seen that at the lowest density [$\rho < \rho_{c1}(T)$], there is a possibility for the ions to move up to a distance $L_M = 20$ – 25 Å for the given time scale (red curve, L_M being defined by $4\pi r^2 G_s(r, t) = 0.01$). The Van Hove function remains nearly unchanged in this density range, indicative of a weak effect of compaction on the dynamics, as also noted from the mild decrease of D_{Na} with ρ (Fig. 3). The dynamics starts to evolve for larger densities and a gradual decrease of L_M is obtained which reduces to less than 5 Å. Ultimately, for, e.g., $\rho = 4.5$ g/cm³, the Van Hove function reduces to a single sharp peak (blue curve) centered at around 1.83 Å, corresponding to a distance somewhat lower than the Na-O distance (2.36 Å,³⁹ i.e., sodium atoms only oscillate between different neighboring positions inside a given pocket. Hence, we conclude that on a given time scale (here 20 ps), with decreasing density, sodium atoms will first display only cagelike motions with back-and-forth hops, and then, as ρ decreases, they experience distances that are larger than simply the spatial extent of a pocket (from Fig. 1, typically 6 Å), and will ultimately be able to cover long distances along ionic pathways as $\rho < \rho_{c1}(T)$.

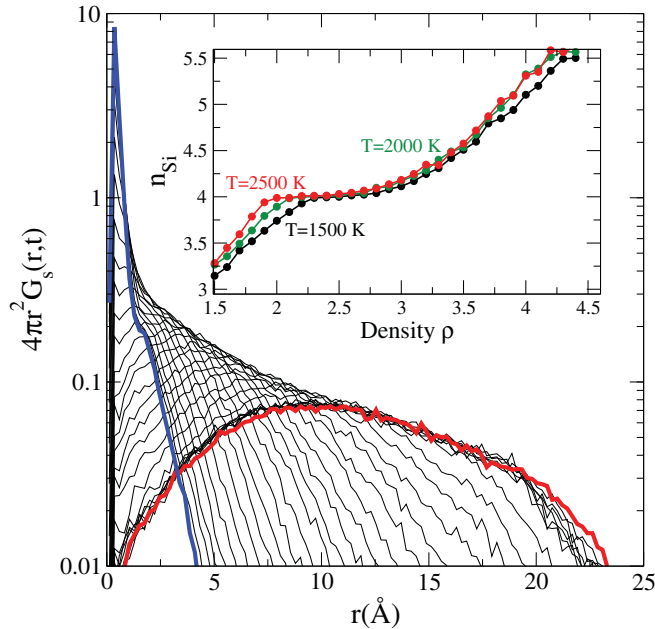


FIG. 4. (Color online) Van Hove function $G_s(r,t)$ of the NS3 system at 2000 K and fixed time $t = t_0 = 20$ ps for various densities between 2.0 and 4.5 g/cm³. The red and blue curves correspond to 2.0 and 4.5 g/cm³, respectively. The inset shows the change in Si coordination number n_{Si} as a function of density for three selected temperatures.

IV. DISCUSSION

We find a clear correlation with structural changes as seen from the inset of Fig. 4. The threshold density $\rho_{c(1)}(T)$ coincides indeed with the density at which the silicon and oxygen network becomes respectively four- and twofold connected. This correlation can be clearly established when temperature changes are considered. Indeed, the threshold density $\rho_{c(1)}(T)$ found for D_{Na} is found to shift to lower densities when the temperature is increased (broken line in Fig. 2), consistently with the obtained corresponding shift of the density at which Si and O become respectively four- and twofold connected. For lower densities, we find a stretched melt, i.e., there is a constant decrease of the network connectivity which does not hinder mass transport as D_{Na} is found to be nearly constant. For densities larger than $\rho_{c(1)}(T)$, however, the silicon coordination number grows to values larger than 4, whereas a small increase of n_O is found (to 2.3 at 4.4 g/cm³). The additional interactions (via the increase of n_{Si}) appearing on densification must contribute to the decrease of the Na motion as more energy is needed in local deformations in order to create pathways for the ionic migration.

The fraction of Na atoms that have migrated through the structure can be computed from the Van Hove function $G_s(r,t)$ at a given time, and corresponding results are displayed for the two distances $r_0 = 5$ and 15 Å. At 1500 K and $\rho = 2$ g/cm³, nearly 70% of the sodium atoms have moved by a distance of 5 Å within 20 ps. This fraction falls to less than 10% if a distance larger than the interpocket distance is considered (15 Å) in Fig. 5. Furthermore, one can remark that this fraction is nearly constant for low densities. At $\rho = \rho_{c(1)}(T)$ and low

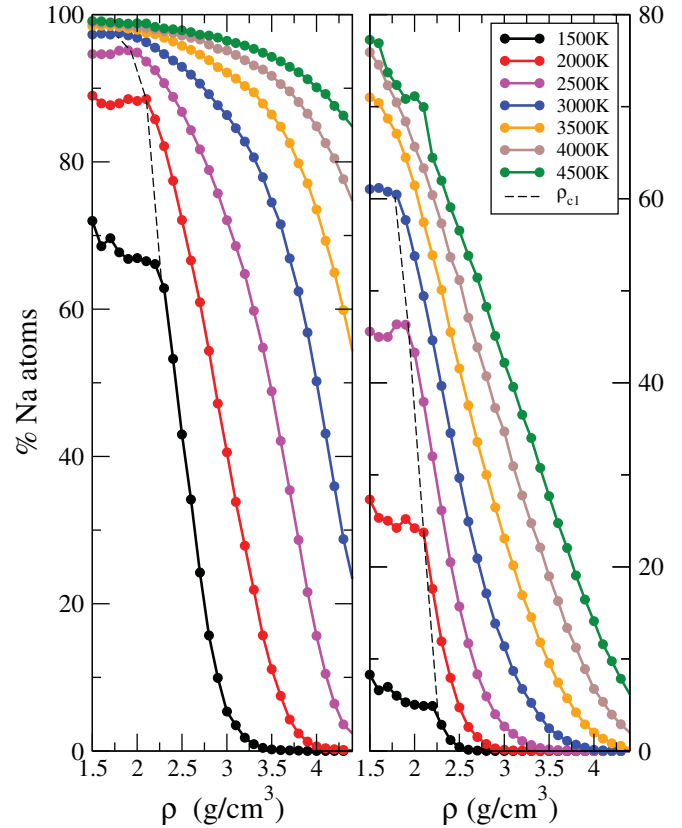


FIG. 5. (Color online) Fraction of Na atoms having moved by 5 Å (left) and 15 Å (right) after 20 ps as a function of density for different temperatures. The broken line represents the density threshold $\rho_{c(1)}(T)$.

temperatures, however, this fraction drops precipitously to zero within a small density range (typically 0.8 g/cm³ for $T = 1500$ K). An increase in temperature leads to a less marked drop but still with a similar trend. It also implies that for glasses ($T < 1500$ K, not studied here because of the numerical limitation that does not allow us to reach the diffusive régime on computer time scales), the change in the dynamics at $\rho = \rho_{c(1)}(T)$ should be even more dramatic as the drop at $\rho_{c(1)}(T)$ increases with decreasing temperature. These results suggest that the Na motion displays a percolative behavior when the density is decreased from, e.g., 4 g/cm³ to $\rho_{c(1)}(T)$ with intrapocket motions being dominant at high density (Fig. 2) as the system is locked by an increasingly connected Si network created by higher coordination numbers (Fig. 4 inset). These pockets connect together in small trees under a density decrease because Na atoms experience larger distances on a given time scale. These trees finally percolate together at $\rho = \rho_{c(1)}(T)$ and lead to the usual channel motion.

In summary, we have shown that the spatial distribution and dynamics of sodium atoms in a silicate system was subject to huge changes with increasing density. While the sodium forms a well-connected network of diffusion channels at low density, these reduce to smaller pathways on increasing ρ and finally reduce to pockets for $\rho \simeq 4$ g/cm³. Threshold behaviors are clearly obtained from the behavior of the sodium diffusion constant D_{Na} with density along different isotherms. These thresholds correlate well with those found from the study of the

network coordination numbers, and the Van Hove correlation function quantifying how the Na atoms evolve through the network structure.

Given the importance of the silicate system in earth sciences and given the fact that such high densities (4 g/cm^3) can be easily achieved at gigapascal pressures that do apply in the Earth's mantle, it is tempting to stress as a conclusion that mass transport in simplified magmas must be sometimes abruptly affected by small density or pressure changes. However, one

has to keep in mind that cation diffusion in real magmas at depth are also very sensitive⁴⁰ to dissolved components such as water or carbon dioxide.

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